



# Study on the internal conversion dynamics following different electron transfer at a donor/acceptor polymer heterointerface



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## ABSTRACT

By constructing a donor/acceptor (D/A) polymer heterointerface, we theoretically study the internal conversion (IC) dynamics following different electron transfer at the D/A interface in the framework of a tight-binding model combined with a nonadiabatic evolution method. We find that different higher-lying charge-transfer (CT) states can form at the D/A interface with the natures determined by the transferred electron energy. As compared with the lowest-lying CT state, these higher-lying CT states are spatially more delocalized and energetically more prone to separate into free charges. By simulating the IC relaxation dynamics of these higher-lying CT states, we find that their timescales are closely related to the transferred electron energy, as well as the D/A interfacial electronic structure. In addition, considering that the IC relaxation dynamics is vibrationally assisted, effect of the vibrational damping on the process is discussed. These researches should be of crucial importance for further understanding the photovoltaic process at a D/A polymer heterointerface, especially the “hot CT mechanism” experimentally suggested to explain the highly efficient charge separation in high-performing D/A polymer solar cells.

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## 1. Introduction

Since the first report of two-layer organic solar cell by Tang in 1986 [1], donor/acceptor (D/A) polymer heterojunction system has become one of the most promising candidates in photovoltaic applications. With the development of the past few years, despite the power conversion efficiency of such a system has approached and even broken 10% [2–4], it still remains far below the thermodynamic limit of a single-junction organic solar cell (>20%) [5]. As such, one of the most critical challenges for polymer solar cells is to further improve the power conversion efficiency. To achieve such a goal, it is essential to get a comprehensive understanding for the photovoltaic process in such a system, in particular the charge separation mechanism at the D/A polymer heterointerface [6,7].

It is known that, due to the strong electron–lattice interaction in polymers, strongly bound electron–hole pairs or excitons are primarily created in these materials after photon absorption [8,9]. Quantitatively, we can introduce binding energy to describe the bound extent of an exciton, the values of which for prototypical

polymers are usually in the range of 0.2–1.0 eV [7,10,11]. As these values are much larger than the thermal energy at room temperature, it is very difficult to dissociate the exciton solely by thermal effect. To achieve efficient exciton dissociation, a D/A heterojunction structure is generally employed in polymer solar cells. In such a system, once an exciton reaches the D/A interface through interchain hopping [12,13] or intrachain migration [14–16], it can be dissociated by the driving force induced by the interface potential [6,7,17–19]. However, most of researches have verified that, after the exciton dissociation, the hole left on the donor and the electron transferred into the acceptor are still bound together across the D/A interface, which is known as a charge-transfer (CT) state [17–25]. Although the value of the binding energy of a CT state is smaller than that of an exciton, i.e., 0.1–0.5 eV [23–26], it remains much stronger than the thermal energy at room temperature. In this regard, charge separation at the D/A interface is still expected to be highly inefficient. However, a surprising fact is that the internal quantum efficiency obtained from the best-performing D/A polymer solar cells can approach and even exceed 90% [27,28], which suggests that, in actual devices the charge separation indeed takes place with a very high efficiency. Therefore, it is crucial to determine how the electron–hole pair overcomes the strong binding energy and the key factors responsible for charge

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separation efficiency in D/A polymer solar cells.

Most recently, it has been suggested that intrachain or interchain delocalization of charge states plays a crucial role in charge separation [18,19,22–25]. Theoretically, by kinetic Monte Carlo simulations and analytic theory, Deibel [29] and Nenashev [18] separately showed that delocalization of charge states along polymer chains can increase the mean distance between the electron and hole at the D/A interface and thus reduce the binding energy. Experimentally, there appear two different opinions about the charge delocalization mechanism. On the one hand, it was indicated that, for some D/A systems (e.g., PBDTTPD/PC<sub>61</sub>BM and PCDTBT/PC<sub>71</sub>BM) the transferred electron or the left hole after exciton dissociation itself has a strong delocalization extent even after a complete relaxation to the lowest-lying CT state (denoted as CT<sub>0</sub> state) [23,24,28]. Such a character ensures a weak binding of the CT<sub>0</sub> state in these systems and charge separation can take place without the assistance of excess energy. On the other hand, it was showed that the dissociation of an exciton at the D/A interface can initially lead to the formation of a hot CT state (i.e., a higher-lying CT state denoted as CT<sub>*n*</sub> state, where *n* = 1, 2, 3, ... indicates the lying energetic level of the transferred electron). The excess energy in the CT<sub>*n*</sub> state is expected to facilitate the delocalization of charge states and consequently results in the efficient charge separation, which is known as the “hot CT mechanism” [30–34].

The “hot CT mechanism” seems to be verified experimentally by Bakulin et al. [32], in which they applied an infrared (IR) photoexcitation to a working polymer photovoltaic diode and thus observed an additional increase of the photocurrent. This finding was rationalized by the fact that the absorbed IR photon can “push” a localized CT<sub>0</sub> state back to a delocalized CT<sub>*n*</sub> state, which is similar in nature to that formed right after the exciton dissociation at the D/A interface, providing an additional channel for charge separation. Despite all this, a crucial issue with the “hot CT mechanism” still exists. As we know, due to the higher energy, in addition to the desirable charge separation, the higher-lying CT<sub>*n*</sub> state will simultaneously relax to the lowest-lying CT<sub>0</sub> state through ultrafast internal conversion (IC) process [34–37]. Therefore, it is expected from the “hot CT mechanism” that charge separation must occur on a timescale comparable to or shorter than the IC relaxation time [6]. In the case of the charge separation dynamics, it has been widely accepted that this process can take place within a timescale of ~100 fs [25,32–34]. However, for the IC dynamics, the reported timescale varies in a wide range from ~60 fs to 1 ps [34,36]. Recently, by using the DFT calculation and the Multiconfiguration Time-Dependent Hartree (MCTDH) method, Tamura and Burghardt elucidated the competition between the IC and charge separation dynamics in a D/A system of P3HT/PCBM [37]. They clarified that the IC relaxations of the higher-lying CT<sub>*n*</sub> states and the excitons formed at the D/A interface can result in their efficient deexcitation, thus profoundly modifying the charge separation dynamics. Especially, they emphasized that the effect strongly depends on the D/A interfacial electronic structure and molecular packing ordering. Based on these considerations, we need to give a further clarification to the timescales of the IC relaxation process of different higher-lying CT<sub>*n*</sub> states, particularly find out a universal law determining their IC relaxation time in different D/A polymer photovoltaic systems.

Here, we aim to address the issues raised above by theoretically studying different electron transfer and relaxation at the D/A polymer interface. Firstly, from a static point of view, we will characterize the natures of different higher-lying CT<sub>*n*</sub> states transiently formed following different electron transfer at the D/A interface in order to determine whether charge separation from

these CT<sub>*n*</sub> states is energetically favorable or not. Subsequently, we will simulate the IC relaxation dynamics from different CT<sub>*n*</sub> states to the CT<sub>0</sub> state and compare the corresponding relaxation time. Finally, taking CT<sub>1</sub> state as a reference state, we will verify some factors affecting the above IC dynamics and try to give a universal law between them.

## 2. Model and method

We construct a D/A polymer heterointerface by choosing two parallel aligned poly(*p*-phenylene vinylene) (PPV) molecules with different on-site energies [17,22], as sketched in Fig. 1, which can be simplified as two coupled one-dimensional chains by a renormalization treatment to the benzene rings [38].

In the framework of an extended version of the Su-Schrieffer-Heeger (SSH) model [39], in which the electron–lattice interaction is emphasized, the Hamiltonian of the system can be written as

$$H = H_1 + H_2 + H_{1-2}, \quad (1)$$

where  $H_j$  ( $j = 1, 2$  shows the chain index) describes an isolated PPV chain, consisting of two parts

$$H_j = H_{j,e} + H_{j,lattice}. \quad (2)$$

$H_{j,e}$  shows the electronic part,

$$H_{j,e} = \sum_n \Delta_{j,n} C_{j,n}^+ C_{j,n} - \sum_n t_{j,n,n+1} (C_{j,n+1}^+ C_{j,n} + C_{j,n}^+ C_{j,n+1}), \quad (3)$$

where  $\Delta_{j,n}$  denotes the on-site energy of an electron at site  $n$ , and  $C_{j,n}^+$  ( $C_{j,n}$ ) the creation (annihilation) operator of an electron at site  $n$ . The second term in Eq. (3) shows the electron hopping between the nearest-neighbor sites along the chain, and the transfer integral  $t_{j,n,n+1}$  between sites  $n$  and  $n + 1$  is written as

$$t_{j,n,n+1} = t_0 - \alpha_j (u_{j,n+1} - u_{j,n}) - t_1 \cos n\pi + t_2 \cos\left(\frac{n+1}{3}\pi\right) \cdot \delta\left(\frac{n+1}{3}, \text{int}\right). \quad (4)$$

$\delta\left(\frac{n+1}{3}, \text{int}\right) = 1$  if  $\frac{n+1}{3} = \text{int}$ , and  $\delta\left(\frac{n+1}{3}, \text{int}\right) = 0$  if  $\frac{n+1}{3} \neq \text{int}$ , where “int” means an integer.  $t_0$  represents the nearest-neighbor transfer integral for a uniform bond structure,  $\alpha_j$  the electron–lattice interaction constant,  $u_{j,n}$  the displacement of a unit at site  $n$ , and  $t_{1(2)}$  the symmetry-breaking parameters introduced to reflect the lattice feature of a PPV monomer.

$H_{j,lattice}$  describes the classical treatment to the elastic potential and kinetic energy of a site and is written as

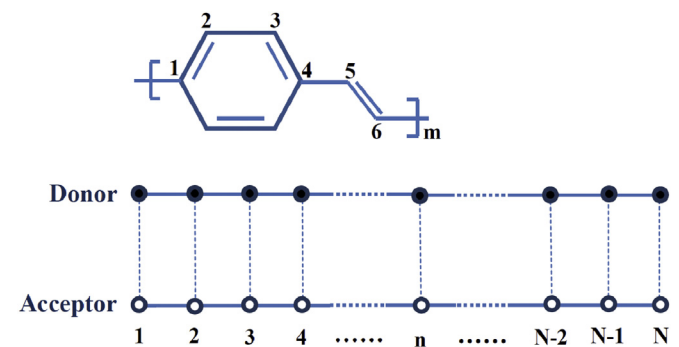


Fig. 1. Schematic diagram of the D/A polymer heterointerface constructed by two parallel aligned PPV chains. The black filled circles and white filled circles separately indicate the lattice sites of the two chains with different on-site energies.

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